PB83-255844

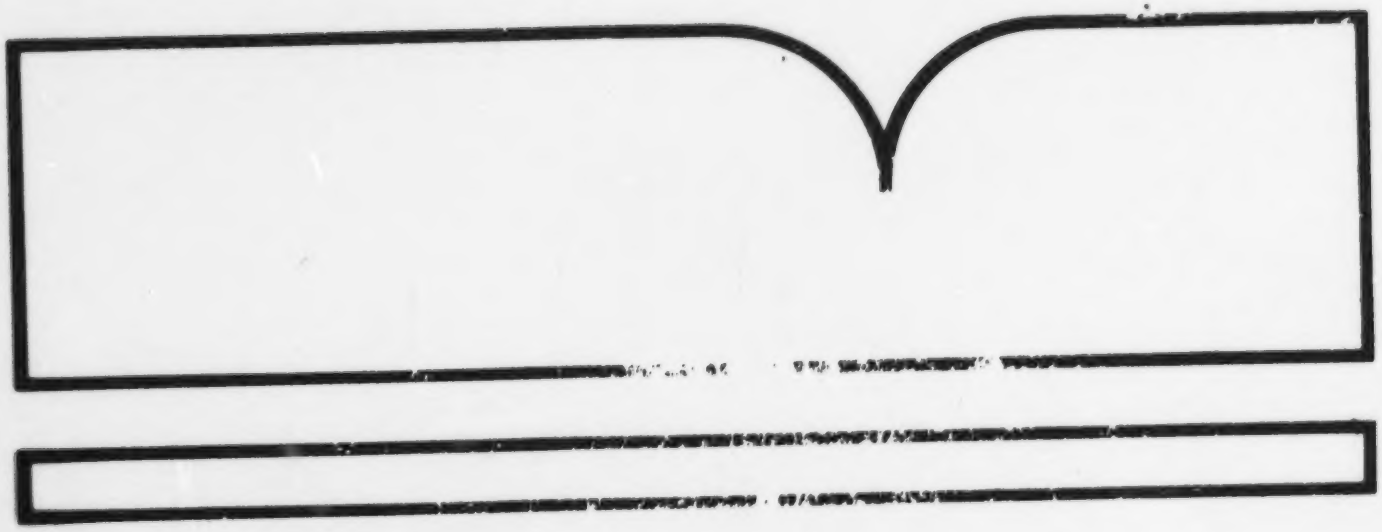
Measurement of Mass Spectra for the EPA (Environmental Protection Agency) Toxic Substances Data Base

Radian Corp., Austin, TX

Prepared for

Environmental Monitoring and Support Lab.
Cincinnati, OH

Aug 83



U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/4-83-036		PB83 255844

4. TITLE AND SUBTITLE	5. REPORT DATE
Measurement of Mass Spectra for the EPA Toxic Substances Data Base	August 1983
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Lawrence H. Keith	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Radian Corporation P. O. Box 9948 Austin, Texas 78766	11. CONTRACT/GRANT NO. Contract #68-03-2879
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Monitoring and Support Laboratory U.S. Environmental Protection Agency Office of Research and Development Cincinnati, OH 45268	Final Report 14. SPONSORING AGENCY CODE EPA/600/06

15. SUPPLEMENTARY NOTES

To be submitted to NTIS.

16. ABSTRACT

A total of 3024 compounds were procured to measure high quality mass spectra for inclusion in the NIH/EPA mass spectral data base. Compounds were assayed for purity before mass spectra were measured and, when necessary, were purified by thin-layer chromatography, recrystallization, sublimation, or distillation. Compounds that were sufficiently volatile to be amenable to gas chromatography (GC) and were less than 99% pure were introduced by GC. Compounds that were ≥ 99% pure and sufficiently volatile were introduced by molecular leak. The direct insertion probe was used for pure but nonvolatile compounds. Quality control procedures included the use of decafluorotriphenylphosphine (DFTPP) for the molecular leak and GC inlets and cholesterol for the direct insertion probe inlet. Spectra of these standards were required to meet stringent acceptance criteria every four hours of instrument operation. High quality mass spectra were measured for 2000 of the 3024 compounds procured.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to Public	Unclassified	34
	20. SECURITY CLASS (This page)	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)

PB83-255844

EPA-600/4-83-036
July 1983

MEASUREMENT OF MASS SPECTRA FOR THE EPA TOXIC SUBSTANCES DATA BASE

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by

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EPA Contract No. 68-03-2879

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Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.
- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.
- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.
- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

Currently, the most useful analytical technique to identify and measure organic environmental pollutants is combined gas chromatography/mass spectrometry (GC/MS), and efforts to enhance its usefulness are continuing. Evaluations of GC/MS identification techniques indicate that the best way to increase the probability of correct pollutant identifications is to expand the library of reference mass spectra. This report documents activities of one project in a continuing effort to expand the number of reference spectra available to the many private and Federal, state, and local government laboratories using GC/MS for environmental sample analyses.

Robert L. Booth, Acting Director
Environmental Monitoring and Support
Laboratory - Cincinnati

ABSTRACT

A total of 3,024 compounds were procured for the purpose of obtaining high quality mass spectra. These compounds were assayed for purity prior to obtaining their mass spectra and, in certain cases, were purified by thin-layer chromatography (TLC), recrystallization, sublimation or distillation. Mass spectra were obtained by a molecular leak if the compounds were 99 percent pure and possessed sufficient volatility. The direct insertion probe was used if the compounds were pure but nonvolatile. The gas chromatographic inlet was used for the majority of the compounds which fell into the category of being volatile enough to be separated by gas chromatography (GC) and less than 99 percent pure. The quality control protocol involved the use of decafluorotriphenylphosphine (DFTPP) for the molecular leak and GC inlets and cholesterol for the direct insertion probe inlet. Spectra of these standards were required to pass stringent acceptance criteria every four hours of instrument operation. High quality mass spectra were generated from 2,276 of the 3,024 compounds procured.

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NOTE: Due to the use of computer printouts for some Figures, some clarity was lost in the reproduction process. Duplicate Figures, which may be clearer, may be obtained from Ann Alford-Stevens, Advanced Instrumentation Section, Environmental Monitoring and Support Laboratory, USEPA, 26 W. St. Clair, Cincinnati, OH 45268.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS:

EPA	- U.S. Environmental Protection Agency
TSCA	- Toxic Substances Control Act
NTP	- National Toxicology Program
TLC	- Thin-Layer Chromatography
DIP	- Direct Insertion Probe
FID	- Flame Ionization Detector
GC	- Gas Chromatography
GC-MS	- Gas Chromatography-Mass Spectrometry
MS	- Mass Spectrometry
MW	- Molecular Weight
torr	- unit of atmospheric pressure, where 760 torr = 1 atmosphere
g	- micrograms
L	- microliters
m/e	- mass to charge ratio
°C	- degrees Centigrade
CI	- Chemical Ionization
EI	- Electron Impact
BPI	- Bytes per inch
NSRDS	- National Standard Reference Data System
ASCII	- American Standard Code for Information Interchange
DFTPP	- Decafluorotriphenylphosphine

SYMBOLS:

$<$	- less than
$>$	- greater than
$\leq$	- equal to or less than
$\geq$	- equal to or greater than

SECTION 1

INTRODUCTION

The Toxic Substances Control Act (TSCA), which became law in 1976, required (among other things) that the U.S. Environmental Protection Agency (EPA) compile a list, or "inventory," of all chemicals manufactured in the U.S. In 1978, when the initial Inventory was compiled, it was determined that of the 43,278 chemical substances it contained, only 3,862 or 8.92 percent were represented in the Mass Spectral Data Base, which then contained 32,187 spectra.

Because the Mass Spectral file serves as a major resource in pollutant identification and because most industrial pollutants are manufactured in or imported into the U.S. and are therefore in the TSCA Inventory, this situation clearly demanded correction. Accordingly, a list of Inventory chemicals absent from the Mass Spectral file was prepared and prioritized by decreasing amount of annual commercial volume. After this prioritized list was available, Radian procured samples of chemicals on the list, assayed their purity, purified them if necessary and, finally, measured their mass spectra. Specifications for all these steps were carefully defined so that high quality mass spectra would emerge from the effort.

SECTION 2

CONCLUSIONS

High quality mass spectra can be produced in large numbers if a carefully controlled and documented program is maintained. A much larger period than is normally estimated is required to locate sources of many of these compounds. This is because many are not commercially available, being intermediates in chemical production, and others are only available from specialty chemical supply sources. Often the chemicals obtained have no indication of purity and, in fact, may contain significant amounts (5 to 25 percent) of impurities. Special considerations must be established prior to receiving large numbers of toxic chemicals to safely handle compounds which:

- are extremely toxic,
- are highly flammable,
- are very volatile,
- are noxious or are lachromators,
- are sensitive to light, air, mositure and/or heat, and
- are not necessarily acutely toxic but which pose carcinogenic or teratogenic risks on exposure.

SECTION 3

EXPERIMENTAL SUMMARY

COMPOUND PROCUREMENT

During the contract period, a total of 3,024 compounds were procured from a list of over 10,000 candidates supplied by EPA. Although it was originally anticipated that a significant portion would come from government chemical repositories and chemical manufacturers, who offer free samples, this was not the case. Many chemicals in various governmental agency repositories were already part of the mass spectral data base and, although some success was achieved in obtaining free samples, it was difficult and time consuming to track down the appropriate person in a given company who could authorize sending a free sample for analysis. In fact, it was cheaper to buy a small quantity of chemical for analysis when that was possible.

However, a total of 193 compounds were obtained from the EPA Repository for Toxic and Hazardous Materials and the National Toxicology Program (NTP) Chemical Repository, both of which are maintained at Radian Corporation. Most of the remaining 2,831 chemicals were purchased from commercial chemical supply houses. A computerized list of the status of each of these compounds was maintained. An example of the data is shown in Figure 3-1 and the abbreviation codes are listed in Table 3-1.

ASSAY METHODS

A total of 3,024 compounds were assayed for purity before their mass spectra were measured. As each compound was assayed, an Initial Assay Data Form was completed and placed in an individual folder along with all analytical data, including chromatograms, for that compound.

The assay method of choice was GC using a flame ionization detector (FID). FI was the detector of choice because of its lower detection capability for many compounds. However, when compounds were known to give poor flame ionization response, thermal conductivity and/or a specific halogen, a nitrogen or sulfur detector (usually a Hall electroconductivity detector) was employed for the analysis. Figure 3-2 shows a typical gas chromatogram and Figure 3-3 shows the corresponding Initial Assay Data Form for this example, carboronylmethyl propionate.

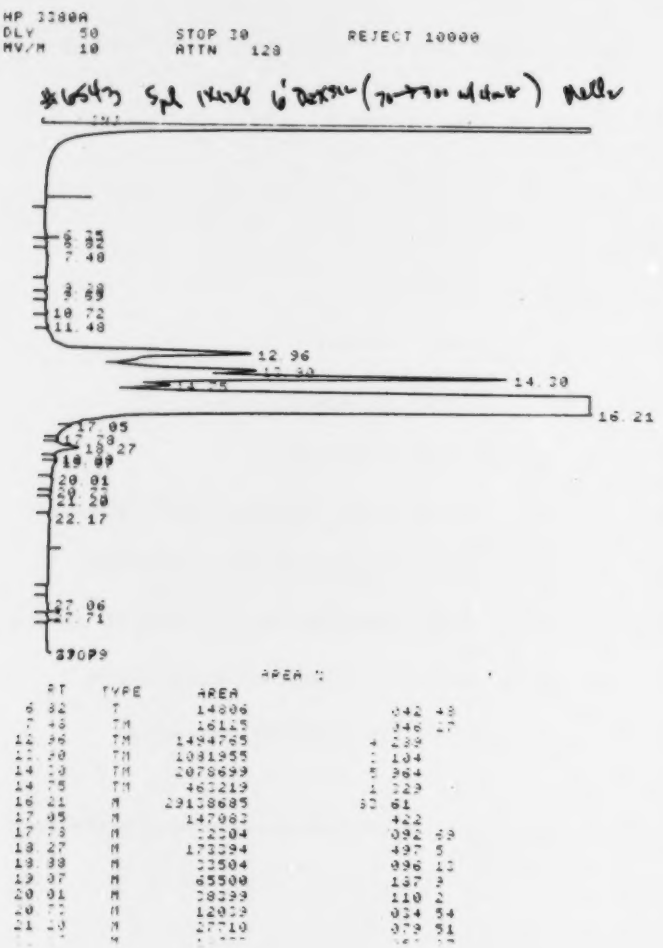
JUNE 16, 1982

	RADIAN#	CAS#	WEIGHT	FORMULA	LOCATION	NAME
192	203	00093-29-8	206	C12H14O3	CI	PHENOL, 2-METHOXY-4-(1-PROPENYL)-, ACETATE (9CI)
193	204	00093-68-5	191	C11H13NO2	MS	BUTANAMIDE, N-(2-METHYLPHENYL)-3-OXO- (9CI)
194	205	00093-69-6	191	C9H13N5	LO	IMIDODICARBONIMIDIC DIAMINE, N-(2-METHYLPHENYL)- (9CI)
195	206	00093-81-2	368	C22H44N2O2	LO	9-OCTADECENAMIDE, N-(2-AMINOETHYL)-N-(2-HYDROXYETHYL)-, 9CI)
196	207	00093-82-3	371	C22H45NO3	LO	OCTADECANAMIDE, N,N-BIS(2-HYDROXYETHYL)- (8CI9CI)
197	208	00093-83-4	369	C22H43NO3	LO	9-OCTADECENAMIDE, N,N-BIS-2HYDROXYETHYL)-, (Z)- (9CI)
198	209	00093-94-7	306	C16H18O6	LO	1,4-BENZENEDIPROPANOIC ACID, B-ETA,,.BETA.'-DIOXO-, DIETHYL ESTER (9CI)
199	210	00094-21-3	188	C11H12N2O	LO	PROPANENITRILE, 3-((4-FURYLPHENYL)METHYLAMINO)- (9CI)

Figure 3-1. Example of the Computerized Compound Status List

TABLE 3-1. ABBREVIATION CODES USED IN THE COMPUTERIZED COMPOUND STATUS LIST

Missing	=	no supplier
LO	=	located
OR	=	ordered
RC	=	received
AS	=	need reassay
PU	=	needs purification
MS	=	in MS laboratory
FM	=	MS sent on tape to Fein Marquart
AC	=	MS acccepted by Fein Marquart
EP	=	sent chemical to Cincinnati at end of analysis
CI	=	hold for chemical ionization
HO	=	hold for further decision



RT	TYPE	AREA	
6.82	T	14806	042 48
7.48	TM	16125	046 27
12.96	TM	1494765	4 288
14.30	TM	1081955	3 104
14.75	TM	2078699	5 964
16.21	M	29138685	83 61
17.05	M	147083	422
17.73	M	32204	092 49
18.27	M	173394	497 5
18.88	M	32504	096 10
19.07	M	65500	187 3
20.01	M	38299	110 2
20.77	M	12073	034 54
21.20	M	27710	079 51

Figure 3-2. A Typical Gas Chromatographic Assay Using FID. Compound No. 6543, Carboronylmethyl proprionate.

RADIAN

TOXIC SUBSTANCES DATA BASE
INITIAL ASSAY DATA FORMS

Name: Carboranylmethyl Propionate

Formula: $C_6H_{18}B_{10}O_2$ MW: 230

Card Identifier (1)	I
Radian # (2-6)	6543
CAS # (7-16)	62706-37-0
Date (17-22)	May 11, 1981
% Purity (23-28)	___ ___ • ___ ___ (FS)
Destination (29-30)	(MS) FU HO Other___
Column (31-38)	SP2250DB SP1240DA (Dexsil) Tenax
Temp Prog (39-48)	70-300 / 8 or ___ (ISO) range / prog. rate / temp
Retention time (49-54) (free field after 54)	___16 • 21___

*MP: ___ - ___ (LIT)
low high

*BP: ___ - ___/___(LIT)

*CO[1]: ( ) Purity & R.T. Estimated

½' Column
4 mi Cold

[1]max of 40 characters, including spaces

Figure 3-3. The Initial Assay Data Form for Carboronylmethyl proprionate.

It was not possible to assay all compounds by GC due to low volatility or thermal instability of some of them. In these cases, TLC proved to be an excellent method for both assaying and purifying many compounds.

TLC was used to screen 167 compounds for purity. From these, 61 were demonstrated to be 99 percent pure (only one spot); these compounds were then submitted to direct insertion probe (DIP) mass spectrometric analysis. In 39 instances, more than one spot was present on the TLC plate but they were completely separated from one another so that the major component could be scraped from the plate, eluted from the sorbent and subjected to DIP mass spectrometric analysis. Nineteen compounds were analyzed this way. This left 62 compounds that had impurities which were not completely resolvable by TLC and were, therefore, rejected.

COMPOUND PURIFICATION

At the request of the EPA Project Officer, additional purifications were conducted on some compounds in this program. The preferred approach for purifying solid compounds involved recrystallization. When recrystallization methods proved to be ineffective, sublimation was then attempted.

The first attempts at purification of liquids involved distillation techniques. Low boiling liquids were distilled at atmospheric pressure, while high boiling liquids were vacuum-distilled. Figure 3-4 shows the Purification and Reassay Form used for these compounds.

As described in the previous section, TLC was also used as a method of purification, as well as an assay method. Similarly, GC was used in the dual role of compound purification and a method for purity assays.

MASS SPECTRAL MEASUREMENTS

In order to obtain high quality mass spectral data, careful attention was given to the methods of sample introduction, the tuning of the mass spectrometer and the background contaminants present in the system.

Three methods were available for the introduction of samples into the mass spectrometer:

- molecular leak inlet,
- direct insertion, and
- gas chromatographic inlet.

Each inlet method offered advantages and disadvantages, which were weighted according to the nature of the sample. For example, the molecular leak inlet provides a constant pressure of the compound in the ion source of

TOXIC SUBSTANCES DATA BASE

PURIFICATION AND RE-ASSAY

NAME: _____

FORMULA: _____ MW: _____

Radian # (3-6) _____

cas # (7-16) _____

Card ID (1- 2) PU

purification date (17-22) _____

method (23-26) SUBL DIST VACD RECL other _____

destination (27-28) ASsay HOld other _____

comment (31-80) _____

Card ID (1-2) RA

re-assay date (17-22) _____

% purity (23-28) __ __ __ . __ __

destination (29-30) MS HOld other _____

column (31-38) SP2250DB SP1240DA other _____

temp prog (39-48) _____/_____or_____(ISO)
range pr. rate temp.

retention time (49-54) __ __ . __ __

(free field after 54)

*MP: _____ - _____ (EXP)
low high

*BP: _____ - _____ / _____ (EXP)
low high pressure

*CO: _____
(comments)
_____

Figure 3-4. Purification and Reassay Form

the mass spectrometer. This constant source pressure provides an opportunity to measure spectra over an extended period of time compared to the chromatographic or direct inlet systems. However, the molecular leak inlet is somewhat limited in scope. Compounds of interest must generally have a vapor pressure of at least 10^{-2} torr at the temperature of operation of the inlet. This requirement precluded the use of the molecular leak inlet for most of the compounds analyzed. Also, because the molecular leak inlet does not always provide adequate fractionation of sample impurities, it is often unsuited for the introduction of impure samples. Similar advantages and disadvantages exist for the direct and chromatographic inlet systems. Therefore, several criteria were employed for the selection of the most favorable inlet system for each of the compounds analyzed.

The rationale that was used for the inlet selection is shown in Figure 3-5. In most cases, when the compound purity was greater than 99 percent and exhibited sufficient vapor pressure, the molecular leak inlet was employed for the mass spectral measurements. If the compound did not have sufficient vapor pressure and was 99 percent pure, the method of choice for introduction was the direct inlet. In cases where sample purity was less than 99 percent, a category in which more than 75 percent of the samples were included, the gas chromatographic inlet was employed for sample introduction.

Figure 3-6 shows an example of the computerized data sheet that accompanied each compound to the mass spectrometry laboratory. The analytical comments were completed by the MS operator as shown.

Of course, not all compounds of reasonable molecular weights can be separated by GC. They may be too polar to be chromatographed or they may be thermally labile and decompose during the chromatography.

Compound No. 9615, hydrindantin dihydrate, is an example of a low molecular weight (MW = 358) compound that produced no peaks when it was subjected to GC (Figure 3-7). The structure of hydrindantin dihydrate was obtained from a search of the Chemical Abstracts Registry and is shown in Figure 3-8, along with accompanying information on molecular formula, CAS Registry Number, index name and synonyms. When subjected to direct insertion probe (DIP) MS analysis, a mass spectrum of the compound was successfully obtained, as indicated on the computerized MS Data Form (Figure 3-9); but the ion current profile (Figure 3-10) indicated an impurity which volatilized prior to the main mass of material on the probe as the temperature of the probe was rapidly raised. Likewise, the resulting mass spectrum (Figure 3-11) showed extra mass fragments that could be indicative of one or more impurities.

After analysis by TLC, the largest spot on the plate was scraped off and eluted with about 20 L of methylene chloride. The eluate was concentrated by evaporation on the tip of a glass bead formed from a melting point capillary tube with one end melted. This glass bead was then placed in the DIP of the

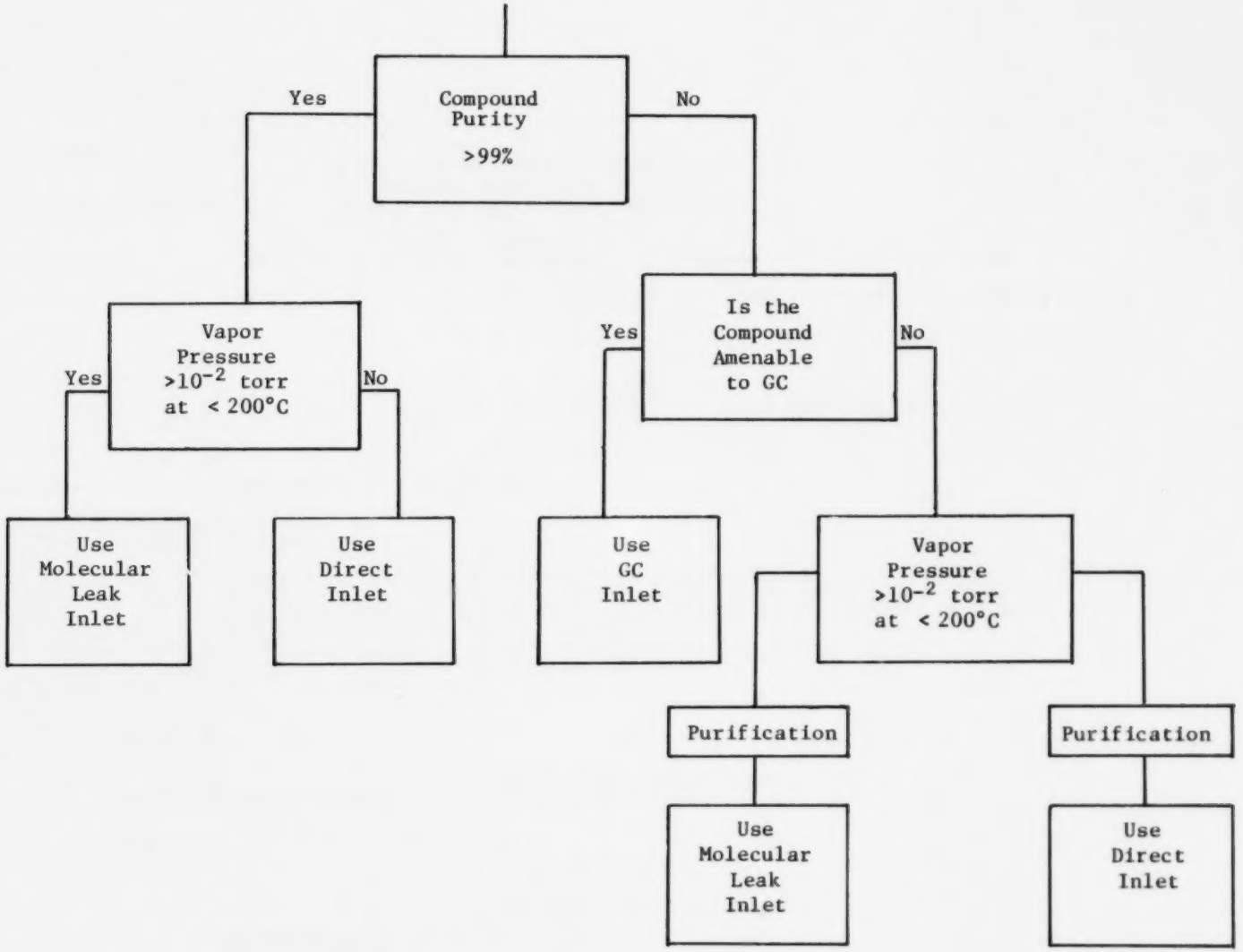


Figure 3-5. Process for the Selection of Mass Spectrometer Inlet System

RADIAN
CORPORATION

*** MSSS CANDIDATE ***

****

IDENTIFIERS*
****

CAS REGISTRY NUMBER: 03252-43-5 RADIAN NUMBER: 12137
FORMULA: C2HBR2N PRIMARY NAME: DIBROMOACETONITRILE

PHYSICAL DATA*
****

DESCRIPTION: CLEAR YELLOW LIQUID
MOLECULAR WEIGHT: 198.86 DENSITY (G/ML): 2.296
MELTING POINT (C): NOT AVAILABLE BOILING POINT (C): 67-69 C @ 24MM
SOLUBILITY: ACETONE: BENZENE:
DMSO: SOLUBLE (>=10 MG/ML @ 27 C) (RAD) ETHANOL: SOLUBLE (>=10 MG/ML @ 27 C) (RAD)
ETHER: WATER: SOLUBLE (>=10 MG/ML @ 27 C) (RAD)
STABILITY: THIS COMPOUND IS STABLE UNDER NORMAL LABORATORY CONDITIONS.

MASS SPECTROMETRY LOG*
****

ANALYSIS: (SUCCESSFUL) UNSUCCESSFUL

DATE: 9-7-82 (AM) PM FRN: 11400 CRN: 65

MASS RANGE: 10-220 RANGE OF COMPOUND SPECTRUM: 67-69 BACKGROUND SPECTRUM: 64

IONIZATION: (EI) CI

INLET: (GC) DIP

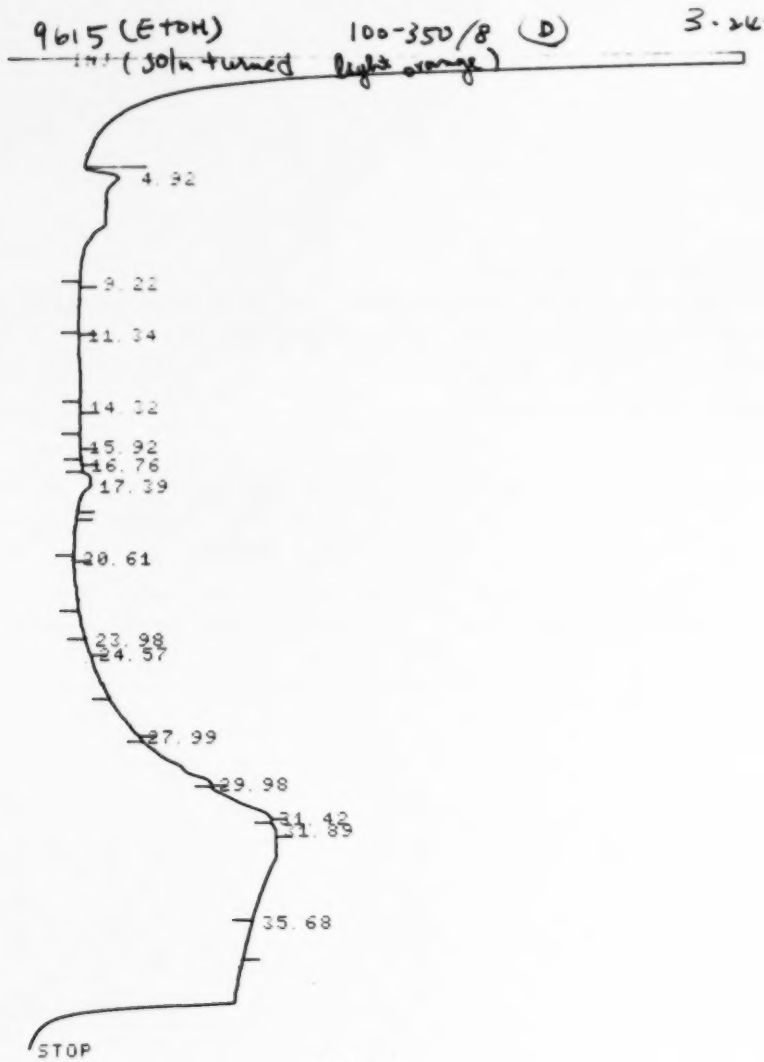
COLUMN: SE-15 DB-5 SE-30 DEXSIL-300 TENAX SP-2250 OTHER: OV-1701

SOLVENT: (METHYLENE CHLORIDE) METHANOL ACETONE DIETHYL ETHER
BENZENE TOLUENE OTHER:

OPERATING CONDITIONS: INITIAL TEMP (C): 40 HOLD (MIN): 1
PROGRAM RATE (C/MIN): 16
FINAL TEMP (C): 280 HOLD (MIN):

COMMENTS:

Figure 3-6. Example of Computerized Data Sheet



	RT	TYPE	AREA	AREA %
	4.92	T	185460	83.49
	14.32	T	10572	4.759
	17.39	T	26104	11.75

HP 3380A
DLY 50 STOP 45 REJECT 10000
MV/M .10 ATTN 22

Figure 3-7. Gas Chromatographic Initial Purity Assay of Hydrindantin Dihydrate

REGISTRY NUMBER = 5950-69-6
INDEX NAME = [2,2'-Bi-1*H*-indene]-1,1'-dione, 2,2',3,3'-tetrahydro-2,2',3,3,3',3'-hexahydroxy- (9CI)
SYNONYM = [2,2'-Biindan]-1,1'-dione, 2,2',3,3,3',3'-hexahydroxy-
SYNONYM = Hydrindantin dihydrate
MOLECULAR FORMULA = $C_{18}H_{14}O_8$

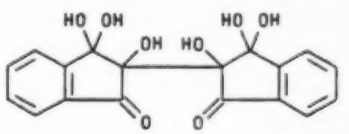


Figure 3-8. Chemical Abstracts Service Data on Hydrindantin Dihydrate

RADIAN
CORPORATION

*** DIP EI/MS CANDIDATE ***
*** 219-028 ***

*** IDENTIFIERS AND PHYSICAL DATA ***

RADIAN# 9615 CAS# 05950-69-6 MW: 358 FORMULA: C18H1408 PRIORITY: ******* LOCATION: MU

NAME: [2,2'-BI-1H-INDENE]-1,1'-DIONE, 2,2',3,3'-TETRAHYDRO-2,2',3,3,3',3'-HEXAMETHOXY- (9CI)

COMPOUND PREPARATION: (NEAT) TLC OTHER:

*** MASS SPECTROMETRY LOG ***

ANALYSIS: (SUCCESSFUL) UNSUCCESSFUL

DATE: 10-27-82 (AM) PM

FHN: 11826 CRN: 58

INITIAL PROBE TEMPERATURE(C): 35 PROBE HEATING RATE(C/MIN): 100

SCAN RANGE: 10-370 COMPOUND RANGE: 63-78 BACKGROUND SPECTRUM: ~~43~~ 44

COMMENTS:

15

Figure 3-9. Computerized MS Data Form for Hydrindantin Dihydrate

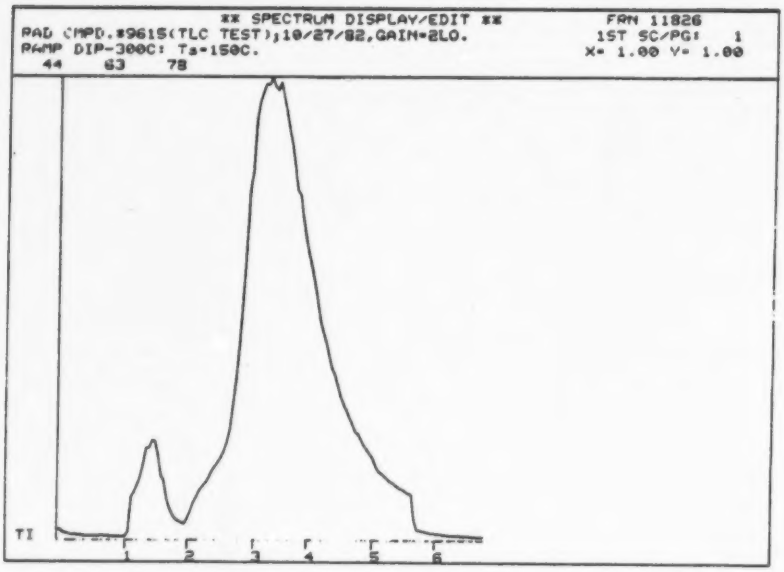


Figure 3-10. DIP-MS Ion Current Profile of Unpurified Hydrindantin Dihydrate

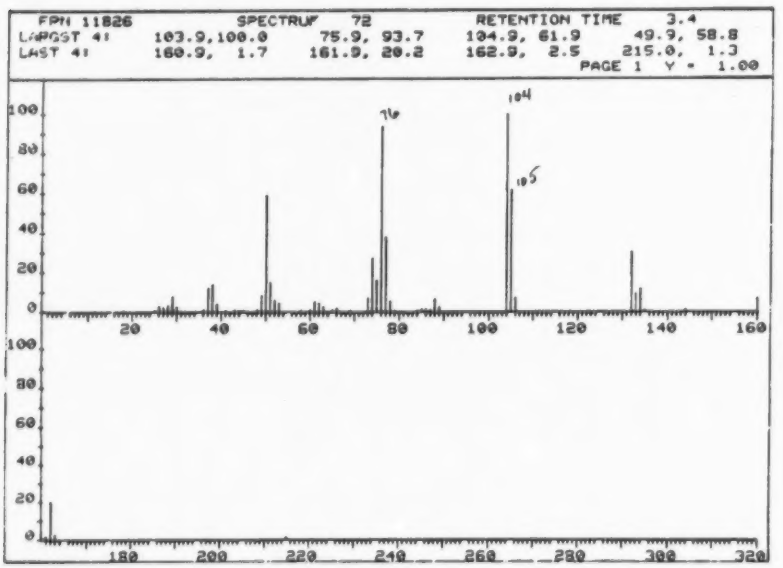


Figure 3-11. DIP Mass Spectrum of Unpurified Hydrindantin Dihydrate

MS and the sample was reanalyzed as before. The resulting ion current profile (Figure 3-12) showed one sharp concurrent volatilization of the material on the bead and produced the mass spectrum shown in Figure 3-13, free of interferring contaminants.

QUALITY CONTROL FOR MASS SPECTRAL MEASUREMENTS

Quality mass spectral measurements can be obtained only through the application of a sound quality assurance program. Therefore, Radian determined the acceptability of the proposed inlet system and the tuning parameters of the mass spectrometer prior to the analysis of all samples. All quality assurance data were forwarded on magnetic tape with each group of actual sample data.

When either the gas chromatographic or molecular leak inlet system was employed for the introduction of a sample, the mass spectrum of the reference compound DFTPP was obtained within the instrument's previous four-hour period. The mass spectrum of the reference compound had to meet the ion abundance criteria summarized in Table 3-2.

For samples analyzed on the direct inlet system, cholesterol served as the reference compound. A suitable mass spectrum for cholesterol included a ratio of ≥ 3 for the ions at m/e 386 and m/e 368 and was obtained within a four instrument hour period prior to the analysis of any samples utilizing the direct inlet system.

The ratio of m/e 386 to m/e 368 ions turned out to be a function of ion source configuration and construction. The ratios were also affected by the temperature of the ion source, the probe tip material, and the solvent that the cholesterol was dissolved in. Table 3-3 gives results of a study of some of these parameters.

CHEMICAL IONIZATION MEASUREMENTS

Forty-two compounds were successfully analyzed by methane chemical ionization (CI) mass spectrometry because electron impact (EI) mass spectrometry did not yield an observable molecular ion.

In order to yield acceptable methane chemical ionization spectra, the proper tuning and ion source parameters of the mass spectrometer were first demonstrated in the EI mode by the analysis of DFTPP. After the quality control criteria were met with the reference compound, the instrumental parameters were changed to accomplish chemical ionization.

Acceptable methane chemical ionization conditions were achieved when the methane spectrum was found to be within ± 20 percent of the following data:

m/e	Relative Intensity
29	100 percent
17	52 percent
41	62 percent

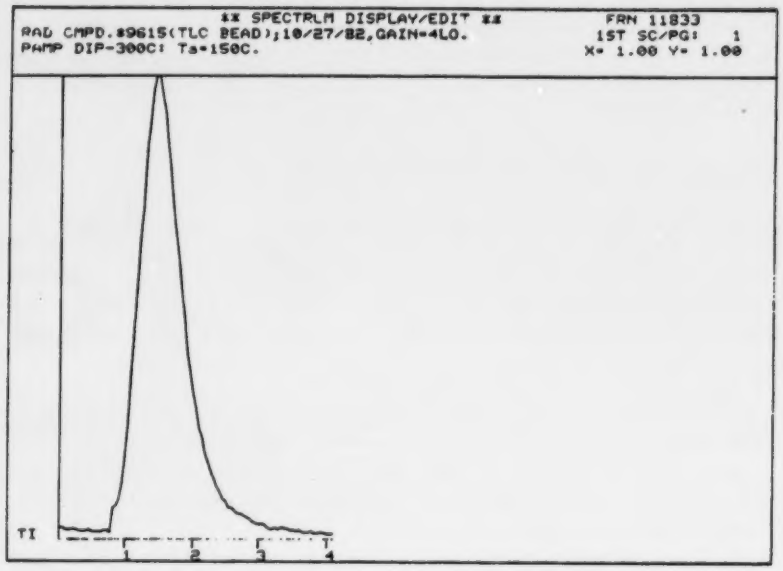


Figure 3-12. DIP-MS Ion Current Profile of Hydrindantin Dihydrate After Purification by TLC

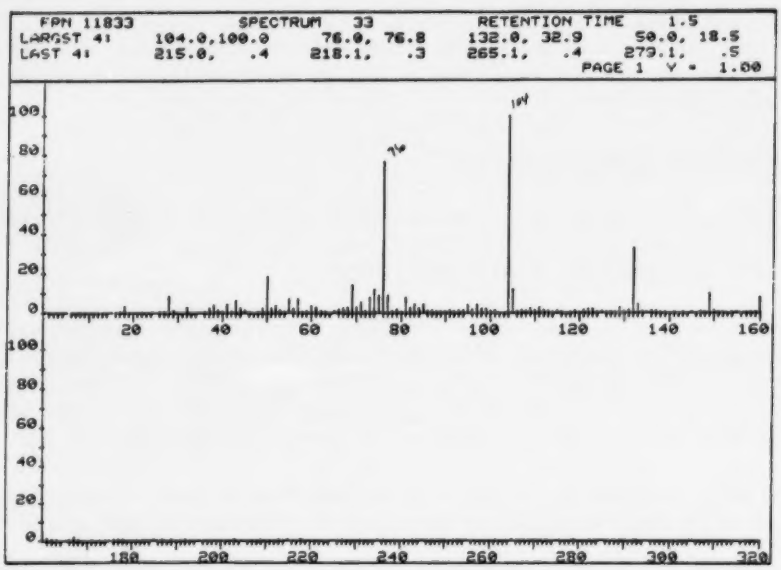


Figure 3-13. DIP-MS of Hydrindantin Dihydrate After Purification by TLC

Table 3-2. QUALITY CONTROL CRITERIA FOR DFTPP AND CHOLESTEROL

Mass	Ion Abundance Criteria
	DFTPP
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% mass of 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	At least 1% of mass 198
441	Less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442
	CHOLESTEROL
43	Base peak, 100% relative abundance
368	Less than 33% of mass 386
386	Greater than 30% of mass 43
387	26-36% of mass 386

TABLE 3-3. DEPENDENCE OF CHOLESTEROL DIP SPECTRAL CHARACTERISTICS ON ANALYTICAL CONDITIONS

ANALYTICAL CONDITIONS[1]			SPECTRAL CHARACTERISTICS			
Probe Configuration	Solvent	Source Temperature (°C)	Base Peak (m/e)	% Intensity Relative Base Peak (m/e) 43	% Intensity Relative Base Peak (m/e) 386	Ratio of Intensity (m/e) 386/ (m/e) 368
Unsilanized glass bead	Acetone	200	105	71	63	2.1
Silanized bead	Acetone	200	107	50	76	1.8
" "	"	170	386	60	100	2.0
" "	"	"	81	80	68	2.5
" "	"	"	81	84	67	2.2
" "	"	"	95	90	32	2.2
" "	"	"	43	100	59	2.1
Silanized bead[2]	"	"	43	100	31	2.3
Extended silanized bead	Acetone	150	81	92	73	2.3
Probe surface	Acetone	150	43	100	39	2.2
Unsilanized wire	Acetone	150	43	100	94	2.5
" "	"	"	386	99	100	2.6
" "	"	"	43	100	99	2.5
Silanized wire	Methanol	150	43	100	78	3.1
" "	"	"	43	100	74	3.0
Resilanized wire	Acetone	150	43	100	55	2.7
" "	Methanol/Water	"	43	100	69	2.6
" "	"	"	386		100	2.7
Silanized wire	None[3]	170	43	100	31	1.8

[1]Sample analyzed on the HP-5982, unless noted

[2]Sample analyzed on the HP-5985

[3]Crystalline material applied directly to probe.

After proper tuning and chemical ionization conditions were demonstrated, sample mass spectral measurements were conducted.

SPECTRAL REVIEW AND DOCUMENTATION

The documentation that accompanied each mass spectrum is specified in the format of the EPA/NIH (NSRDS) mass spectral database. Part of the documentation was provided in hard copy form and part in industry standard nine-track magnetic tape. These documentation requirements are summarized in Tables 3-4.

The purpose of the documentation was twofold: To record the standardized experimental conditions under which the mass spectra were generated, and to allow the calculation of a Quality Index for each mass spectrum. The nine factors that comprise this Quality Index (QI) are shown in Table 3-5. A QI for each mass spectrum was determined by Fein-Marquart Associates under contract to EPA. However, Radian conducted a preliminary review of the mass spectral data and documentation to assure that none of the QI factors were zero and that the documentation was complete.

The elements of Radian's review of the spectral data and documentations were as follows:

- review of the compound assay chromatogram to yield a measured percent purity in excess of 90 percent for the vapor phase that produced the mass spectrum,
- review of the documentation of the MS operating parameters for completeness and consistency,
- verify that the spectra of the QC standard compounds (DFTPP or cholesterol) met their acceptance criteria,
- review the GC-MS chromatogram or DIP-MS graph and the background-subtracted mass spectrum of each compound from the point of view of QI factors (Table 3-5),
- generate hardcopy tables and magnetic tape of background-subtracted mass spectra for submission to the EPA Project Officer,
- review hardcopy tables before submission to EPA, and,
- update computer file after submission to EPA.

TABLE 3-4. HARDCOPY DOCUMENTATION REQUIREMENTS FOR EPA/NIH MASS SPECTRAL DATABASE

1.	sample identifiers (chemical name, CAS registry number, molecular weight and molecular formula),
2.	date of measurement,
3.	purity assay information,
4.	manufacturer and model of mass spectrometer,
5.	type of inlet system and temperatures of critical inlet system areas,
6.	ion source pressure and reactant gas for chemical ionization spectra,
7.	inlet pressure for samples introduced with molecular leak,
8.	ion source temperature,
9.	resolution at highest mass recorded,
10.	electron ionization energy,
11.	associated QC standard mass spectrum, and
12.	time since last MS calibration.

TABLE 3-5. DESCRIPTION OF QUALITY FACTORS USED TO DETERMINE MASS SPECTRUM QUALITY INDEX

Factor	Feature Tested	Description
QF1	Electron voltage	If $100 > v \geq 50$, QF1 = 1; if $V < 50$, QF1 = $(V-10)/40$, where V = electron ionization voltage.
QF2	Masses above the molecular weight (MW)	QF2 = $\frac{(M+5) - 21}{M+5}$, where M = intensity of molecular ion and I = sum of intensities of all ions with masses greater than MW + 3 + N, where N is 2 for compounds containing bromine or chlorine, 0.5 for compounds containing sulfur or silicon, and 0 for all other compounds.
QF3	Illogical neutral losses	For compounds not containing silicon chlorine or bromine, losses of 2 to 14 amu are not expected; when such losses are observed, QF3 is decreased from a maximum value of 1 in proportion to observed intensities of illogical losses.
QF4	Isotopic abundances	If observed, isotopic abundances vary significantly from calculated values, QF4 is reduced from a maximum value of 1.
QF5	Number of masses	QF5 = N/(Z + 15), where N = number of masses in spectra, and Z = number of atoms in molecule.
QF6	Low mass region	QF6 = (M - M')/(M-39), where M = molecular weight, and M' = lowest reported mass.
QF7	Sample purity	QF7 = P/100, where P = percent purity of compound measured, except if P is less than 90 percent, QF7 = 0
QF8	Time since calibration	QF8 = 1 until time lapse since calibration exceeds one week; thereafter, QF8 is decreased in proportion to elapsed time.
QF9	Calibration spectrum	The similarity index of the calibration spectrum compared to the standard library spectrum of that same compound QF9.

Corrective action was initiated when the spectrum of the QC standard compound or the sample did not meet the acceptance criteria. Corrective actions included the following options:

- o review the MS chromatogram relevant to the choice of the spectrum for background-subtraction,
- o review the MS chromatogram relevant to the choice of selecting the spectral region most characteristic of the compound, or
- o remeasure the mass spectrum after additional purification or by a different inlet.

This procedure of spectral review and corrective action resulted in the generation of high quality mass spectral data for the NIH/EPA database, verified by the high acceptance rate after testing by Fein-Marquart Associates.

DOCUMENTATION OF MASS SPECTRAL DATA ON MAGNETIC TAPE

Compound spectra judged reasonable by the mass spectrometrist were transferred to magnetic tape using the Hewlett-Packard software AASAV. This transfer tape contained binary data representing the complete mass spectral analyses of candidate and tuning compounds. Selected spectral scans for each compound were averaged and a background spectrum subtracted on a Data General ECLIPSE using software written at Radian. The resulting ion intensities were tabulated for internal review. In addition to the compound spectrum, pertinent identifiers (such as CAS number, compound formula and molecular weight) were supplied for each compound. This information was retrieved from a compound inventory database maintained on the ECLIPSE.

Spectra that passed the internal review process were included on tapes sent to EPA. The magnetic tape format was identical to the National Standard Reference Data System (NSRDS) mass spectral tape format shown in Table 3-5. Standard industry compatible nine-track magnetic tapes were used and were all recorded at a density of 800 BPI. Data were recorded on the magnetic tape as a combination of ASCII characters and two's complement binary numbers. Each physical record had a fixed record length of 4,000 bytes. Records with less than 4,000 bytes of usable data were padded with blank characters to achieve a length of 4,000 bytes.

Prior to the delivery of each magnetic tape to EPA, the entire contents of the magnetic tape were printed for verification and quality control. Deliveries of data consisted of a magnetic tape and two hardcopies of the tape contents.

SECTION 4

SUMMARY OF ACCOMPLISHMENTS

The following list of accomplishments are provided as a statistical summary of the work conducted during the 3.25 years term of this contract.

TABLE 4-1. SUMMARY OF ACCOMPLISHMENTS

Number of Candidate Compounds:	13,281
Number of Compounds Procured:	3,024
Number of Compounds Assayed and/or Mass Spectra Obtained:	3,024
Total Number of Mass Spectra Generated:	3,810
Total Number of Mass Spectra Submitted to Fein-Marquart:	2,508
Total Number of Mass Spectra Accepted by Fein-Marquart:	2,506
Total Number of Compounds for which Spectra were Obtained:	2,276
Number of Chemical Ionization (CI) Mass Spectra Generated:	91
Number of CI Mass Spectra Submitted to Fein-Marquart:	42
Number of TLC/Direct Insertion Probe Mass Spectra Generated:	19
Number of Other Direct Insertion Probe Mass Spectra Generated:	400
Number of GC-Mass Spectra Generated:	3,391
Number of Compounds Failing GC Analysis and Recycled via TLC:	167
Number of DFTPP Quality Control Spectra Submitted:	211
Number of Cholesterol Quality Control Spectra Submitted:	22
Number of Chemicals Not Amenable to MS Analysis:	87
Compounds with Unsuccessful Assay/Purifications:	383
Compounds with Unsuccessful MS Analyses:	136
Compounds with Unsuccessful Internal Review:	139
Compounds Rejected by Fein-Marquart Review:	3
Total Number of Unsuccessful Compounds:	748